sion of a trace of air. In 20 hours nearly 3 grs. of silver were volatilised. The deposit of silver was detached without difficulty from the glass in the form of brilliant foil.

III. "A Study of the Planté Lead-Sulphuric Acid-Lead Peroxide Cell, from a Chemical Stand-point. Part I." By G. H. ROBERTSON. Communicated by Professor ARMSTRONG, F.R.S. Received May 27, 1891.

(Abstract.)

The author, in the introduction, states that though, since Frankland in 1883 published his first "Contribution to the Chemistry of Storage Batteries," the capabilities of the Planté cell have been well tested and are now thoroughly understood, there is still considerable uncertainty as to the precise nature of the chemical changes which attend their use; and that it was principally to study the part played by the electrolyte that the investigation, the results of which are recorded in this paper, was instituted about a year ago at the Central Institution at Dr. Armstrong's suggestion, as McLeod's observations on the electrolysis of sulphuric acid solutions led to the supposition that the changes occurring in the acid were probably less simple than was commonly supposed. This supposition was verified.

The first section of the paper deals with the nature of the lead salt formed during discharge. It is pointed out that, as is well known, red lead varies considerably in composition, generally containing a smaller proportion of peroxide than is represented by the formula $Pb_3O_4 = PbO_2 2PbO$; and that with nitric acid it behaves as though it were a mixture of the two oxides, the nitric acid always dissolving out the monoxide. There is no reason why sulphuric acid should not behave similarly, and, since lead sulphate is but very slightly soluble, red lead may be expected always to yield a corresponding sulphate, *i.e.*, a mixture of peroxide and sulphate, containing an amount of sulphate corresponding to the amount of monoxide originally present in combination with the peroxide. At Dr. Armstrong's request a number of experiments were made at the Central Institution (long prior to the reading of Messrs. Gladstone and Hibbert's papers) by two students, Messrs. Briggs and Ingold, on various samples of red lead, with the result that the sulphate formed always corresponded to the monoxide originally present.

As no proof of the existence of a definite homogeneous sulphate corresponding to red lead can be afforded by analysis alone, evidence must be obtained that the product differs in some of its properties from a mixture.

It was to be expected that the E.M.F. of an oxysulphate would differ from that of a corresponding mixture of sulphate and peroxide, and have some definite value; therefore pastes were made of peroxide of lead, peroxide of lead and sulphate in the proportions of 1 to 1 and 1 to 2, and also from the product obtained by treating red lead with dilute sulphuric acid (1 to 5). Experiments made with these pastes showed that there was a difference of degree only between the red lead pastes and the mixtures, and that the lowering of the E.M.F. appeared to depend rather on the intimacy of the mixture, and consequent thorough coating of the peroxide granules with sulphate, than on the proportion of sulphate present.

Mr. Desmond Fitzgerald had already shown, in 1887, at the Institution of Electrical Engineers, that the mere admixture of lead sulphate with peroxide of lead produces a lowering of the E.M.F.

With regard to Frankland's observations respecting the colour of the product formed on the peroxide plate during discharge and the reducibility of the sulphate, the author points out that the colour is due to the incomplete reduction of the peroxide, owing probably to the almost complete blocking up by lead sulphate of the pathways by which the current travels through the electrolyte in the paste; that careful examination of the plugs from a discharged cell shows that the base consists of practically unaltered peroxide of lead, and that the surface, which is rich in $PbSO_4$, is really a mass of partially reduced granules of peroxide of lead which are coated with sulphate.

Also, though pure lead sulphate is very difficult to reduce, it is very well known that mixtures of lead sulphate and peroxide of lead, or other conducting substances, are reduced with comparative ease, and it is very intimate mixtures of this nature which have to be dealt with as a rule in charging a cell.

In conclusion, the author points out:—

That neither chemical nor electrical tests give any ground for supposing that any other sulphate than the ordinary white $PbSO_4$ is concerned in the interactions occurring in the cell;

That were the sudden lowering of the E.M.F. caused by a change in the nature of the chemical compounds formed on the plates, it is very difficult to account for the very rapid recovery of the E.M.F. exhibited by an apparently discharged cell.

In the second section the electrolyte is dealt with, and, after referring to the work of Berthelot, Richarz, Schöne, Traube, and others on the electrolysis of sulphuric acid solutions, the author describes experiments made to test the effect of the addition of sodium sulphate to the electrolyte, as, from information received from Mr. Barber Starkey, it seemed probable that the different behaviour of cells containing sodium sulphate was due to the catalytic action of this salt on the hydrogen dioxide always found in electrolysed acid of the

strength used in batteries, and which is probably formed by secondary action from persulphuric acid.

Mr. Preece most kindly aided the investigation by allowing experiments to be carried out at the General Post Office, where one-half of the secondary cells contain 1 per cent. of sodium sulphate and the other half ordinary dilute acid, sp. gr. 1180. He also put at the disposal of the author the records of the behaviour of the cells, and as they showed that there was much less sulphating with sodium sulphate, as shown by the sp. gr. never falling to the same extent as in the plain cells, but that the general character of the changes in temperature and in sp. gr. during charge and discharge were the same in both types of cell, and of the nature which the work of Professor Ayrton and others has rendered familiar to all, it was only the distribution of temperature and of sp. gr. which was investigated, and this was found to be very irregular.

It was found that the addition of sodium sulphate, in about the proportion of 1 per cent., to freshly electrolysed acid, or during electrolysis, always produced a diminution in the total quantity of "active oxygen," and brought the amount present in the plain cells down almost exactly to that found in the sodium sulphate cells.

Experiments on the growth of the "peroxides" were carried on during five charges and discharges, but only the figures relating to the first discharge are given, as the other charges and discharges are mere repetitions. The peroxides form at once, then undergo a diminution, and then increase again. The alteration in the totals is due mainly to actions occurring at the lead plate in the plain cell, as at the peroxide plate the amounts steadily increase; in the sodium sulphate electrolyte there is a diminution at both plates, followed by an increase.

Determinations were made of the amounts of "active oxygen" present as persulphuric acid and hydrogen dioxide respectively, and it was established that acid taken from the cell reduced peroxide of lead. The presence of hydrogen dioxide being thus established both directly and indirectly, its effect on the E.M.F. of a cell was tested. It was found that, while its addition to the acid in the case of a lead peroxide couple in dilute sulphuric acid produced an annulment or reversal of the E.M.F., the introduction of hydrogen dioxide into the body of the peroxide paste produced an increase of E.M.F. in the case of a platinum-lead peroxide couple.

The latter experiment was made with a view of reproducing, if possible, the conditions of a cell which is started discharging directly it is fully charged, and in which the persulphuric acid formed at the positive during charge may be supposed to break up with the formation of hydrogen dioxide on the cessation of the charging current, thereby increasing the normal E.M.F. of the cell.

The cause of the pink colour of the acid noticed by Mr. Crompton and others was investigated, and found to be permanganic acid, formed probably from the manganese present in commercial lead.

In conclusion, the author points out:—

That "peroxides" are found in appreciable quantities in the electrolyte during charge and discharge;

That their influence must not be neglected in considering the behaviour of the Planté cell;

And that it is to the electrolyte rather than to the plates that attention must be directed if any considerable improvement is to be effected.

IV. "A Study of the Planté Lead-Sulphuric Acid-Lead Peroxide Cell, from a Chemical Stand-point. Part II.—A Discussion of the Chemical Changes occurring in the Cell." By H. E. ARMSTRONG, F.R.S., and G. H. ROBERTSON. Received June 4, 1891.

(Abstract.)

The authors arrive in this paper at the following conclusions:—

1. That the cooling observed in the Planté cell can only be explained as resulting from the dissociation of the dilute sulphuric acid; and as the values given by Messrs. Ayrton, Lamb, Smith, and Woods are in practical agreement with those calculated on the assumption that the acid used is sulphuric acid itself, H_2SO_4, that in all probability such acid and not the dilute acid contained in the cell is operative throughout.

2. That the observed loss in efficiency cannot be due to temperature changes, as these arise through actions occurring out of circuit.

3. That it is difficult from a comparison of calculated with observed values of the E.M.F. to arrive at any final conclusion as to the exact nature of the changes which take place in the cell. On the assumption that sulphating occurs at both plates in circuit and under the influence of H_2SO_4, the calculated value is considerably too high; while, if sulphating occur only at the lead plate, the value calculated is far too low.

4. That a counter E.M.F. of about 0·5 volt would account for the observed departure from the highest calculated value. As peroxides are always present in the electrolyte, it is conceivable that such a counter E.M.F. may exist; moreover, there is also the possible influence of the lead support to be considered.

5. That the observed loss of efficiency is to be attributed to the formation of peroxides in the electrolyte, and to the excessive sulphating occurring chiefly at the peroxide plate in the local circuit existing between the support and the paste.